

## **Section VII.**

# **US SOLAS Working Group 4 Report: Atmospheric Impacts on Marine Biogeochemical Processes**

## **VII.1 INTRODUCTION**

Climate and environmental change will impact marine biogeochemical processes and chemical exchange between the ocean and atmosphere. Climate shifts and feedbacks will affect the thermal structure and current patterns of the upper ocean, changes that will result in cascading effects. These will likely include alterations in the distribution patterns of phytoplankton, their primary production and capacity to export carbon to the ocean's interior, in the production and consumption of climate relevant compounds (CRCs) by the upper ocean pelagic food web, and in the flux between the sea and the atmosphere of dimethylsulfide (DMS) and other CRCs. Subsequent oxidation of DMS to sulfate aerosol will affect aerosol optical depth and cloud albedo. Changes in phytoplankton concentration can affect absorption of solar radiation at the ocean surface and, hence, the heat flux between the atmosphere and ocean. Such processes provide a direct feedback to physical and biological processes in the upper ocean.

Changes in climate can also lead to alteration in the quantity and delivery pattern of mineral aerosol and associated nutrients, such as iron, to the ocean. In regions where iron limits primary productivity, shifts in dust deposition will also contribute to alteration in food web structure and the intrinsic capacity of these systems to biologically sequester atmospheric CO<sub>2</sub>, as well as in changes in the flux of biogases from the ocean. Similarly, atmospheric inputs of fixed forms of nitrogen to the ocean as a result of increasing population and industrialization will lead to increased eutrophication in coastal areas with the possibility of some perturbation (e.g. productivity increases and food web alterations) in more remote oligotrophic ocean areas.

Climate change may also lead to changes in the fluxes of reactive particles and gases from the ocean to the atmosphere. Sea-salt particles can release gases and provide surfaces for heterogeneous chemical reactions. Many of the marine biogases are photochemically active, and changes in their emissions can lead to changes in the radiative environment, chemical cycles, acidity and oxidation capacity of the atmosphere. These complex and interdependent processes can only be addressed by studying both the ocean and the atmosphere and their interactions in a series of joint and coordinated efforts.

## **VII.2 SCIENCE GOALS**

Fluxes across the air-sea interface are bi-directional, and our research questions and goals can be grouped into two broad categories: the effects of atmospheric inputs on key upper ocean biological, chemical and physical processes, and the reciprocal effects of the upper ocean on processes in the lower atmosphere. A crucial implicit objective will be to identify the important feedbacks occurring across this interface.

### **1. Response of the upper ocean to atmospheric inputs: How is a key integrative index of inorganic nutrients and biological processes in the surface ocean, the nitrogen to phosphorus (N/P) ratio, related to atmospheric fluxes?**

The atmosphere serves as a vital conduit of elements from the terrestrial to the oceanic realm. Materials transferred by this route include nutrients that may promote growth of organisms residing in the upper ocean as well as elements and compounds that have negative effects on the oceanic biota. These inputs directly influence the ocean's capacity to assimilate, and to biologically sequester, CO<sub>2</sub> and can affect the flux of CRC between the ocean and atmosphere.

In particular, the relative availability of inorganic nitrogen and phosphorus (often represented as the N/P ratio) is an important property of marine ecosystems with direct relevance to the biological productivity of the upper ocean. The longstanding interest in N/P ratios has largely focused on the interactions between surface plankton and deeper waters (Redfield, 1958; Falkowski, 2000). Redfield (1958) pointed out that the ratio of nitrate to phosphate in deep water was remarkably close to the average composition of surface plankton, and that deep-water ratios were largely defined by the decomposition of sinking detrital material. While the ratio of regenerated nitrate and phosphate in deep water has been found to be relatively constant, subtle differences do exist across ocean basins. In fact, through much of the surface ocean, nitrate and phosphate are delivered to surface waters from depth in a ratio that is slightly less than that required for phytoplankton growth (often given as the canonical Redfield value of about 16:1) (Fanning 1992). Hence, the growth of phytoplankton in much of the world's oceans appears primarily constrained by the availability of inorganic nitrogen.

N<sub>2</sub> fixation and denitrification antagonistically affect the fixed N inventory of the ocean. The deficit in N, relative to P (and with respect to plankton needs) in deep waters (see above) may reflect an excess of denitrification relative to N<sub>2</sub> fixation in the current ocean that contributes to the chronic N limitation through most of the surface ocean. The apparent relative paucity of fixed N is puzzling. If the oceans are largely N limited, why is N<sub>2</sub> fixation not more prominent? What limits the extent of N<sub>2</sub> fixation, and why does denitrification apparently exceed N<sub>2</sub> fixation in the present ocean?

The relative availability of nitrogen and phosphorus in the surface ocean can also be both directly and indirectly affected by atmospheric inputs. These inputs can directly impact surface primary production, biogeochemistry and CRC production. Furthermore, the chemical character and quantity of nutrient inputs through the atmosphere to the surface ocean are likely to change in the near term with climate shifts.

#### ***A. What controls the temporal and spatial patterns of the atmospheric fluxes?***

Most of the atmospheric mineral matter (dust) that contains iron is generated in the arid regions of the world, and in general the highest atmospheric concentrations of dust over marine areas are found over the tropical North Atlantic, the northern Indian Ocean including the Arabian Sea, and the western North Pacific, reflecting their arid source regions upwind. (Husar et al., 1997). The pattern and magnitude of delivery of the dust varies dramatically with season, vegetation cover, topography and soil aridity in the source area and the climate history of the region. It is thus dependent on natural climate variability and human land disturbance as well as future climate change. For example, the historical record as revealed in ice cores suggests that significant increases in dust delivery to the ocean took place during the last glacial maximum, when the earth was colder and drier (Martin 1990, Petit et al. 1999). This appears to be correlated with reduced atmospheric CO<sub>2</sub> content enhanced concentration of atmospheric sulfur species, increased ocean productivity (as measured by total organic carbon [TOC] and biomarkers in marine sediments) as well as a lighter <sup>15</sup>N signature in preserved organics (Ganeshram 1995, Altabet et al. 1995, Farrell et al. 1995). Paleovegetation data and desert deposition data suggest that the last glacial maximum had larger desert areas due to lower precipitation and perhaps lower CO<sub>2</sub> (e.g. Mahowald et al., 1999; Harrison et al., 2001). Similarly, shorter term changes in precipitation patterns, e.g., in the Sahel region in west Africa, have also resulted in significant changes in the transport of mineral dust to the tropical North Atlantic and Caribbean (Prospero & Nees, 1986, Moulin et al. 1997), and there appears to have been an increase in global precipitation over the past century. It is expected that future climate changes will certainly affect dust fluxes to the atmosphere and dust properties; changes in the global wind field and soil moisture will affect the distribution of source areas, the particle size distribution of the generated atmospheric dust, and the overall emission flux of mineral aerosol. This, in turn, would be expected to alter the deposition of atmospheric iron to the ocean. Thus the generation and transport of atmospheric dust and iron in the coming decades could change in important ways depending on future human-derived, as well as natural, climate and other environmental changes.

While we have a rudimentary understanding of the current atmospheric deposition patterns of inorganic nitrogen to the ocean, the primary locations of the input of atmospheric nitrogen to the ocean may change in the near future. Galloway *et al.* (1994, 1995) have evaluated the near-current (1990) fixed nitrogen

generated from human activities such as fossil fuel burning (primarily as nitrogen oxides) and fertilizer use, and the estimated fixed nitrogen that will be produced in 2020 as a result of human activities. Developed regions of the world are predicted to show relatively little increase in the fixation of nitrogen over this time period, while rapidly developing areas will contribute significantly to increased human-derived fixed nitrogen. For example, Asia is predicted to account for ~40% of the global increase from energy-derived fixed nitrogen and ~87% from fertilizer! Both energy sources (nitrogen oxides, and ultimately nitrate) and fertilizer (ammonia, urea) will drive this increase. Significant increases in the atmospheric delivery of nitrogen downwind of these enhanced source regions are expected.

Also, the forms of atmospherically deposited nitrogen (AD-N) are changing (relative to each other). For example, in regions experiencing agricultural expansion and changing land-use practices that include animal-intensive industries (i.e., industrial-scale hog farms), ammonium is becoming more prevalent, while  $\text{NO}_x$  may actually be decreasing (due to emission controls). A relevant and important question is: what are the biogeochemical and trophic impacts of changing composition of AD-N in coastal and open ocean waters? For example, is there a link between harmful algal bloom expansion and an increase in ammonium deposition? The 1985-1989 vs. 1995- 1999 National Atmospheric Deposition Program (NADP) summary indicates a very large increase in ammonium deposition relative to  $\text{NO}_x$  in the US.

Some chemical compounds do not have significant direct terrestrial or oceanic sources compared to in situ atmospheric sources. An example is nitric acid (or nitrate) that results from the gas-phase oxidation of  $\text{NO}_x$  in the atmosphere. The primary source of other atmospheric chemical compounds is terrestrial and/or oceanic emissions (e.g., phosphate, ammonia/um). Although much of the current interest is on iron and dust, it is important to recognize that the atmosphere is a source or a transport path for many different nutrients (e.g., nitrate, ammonium, organic nitrogen compounds, phosphate, Zn) and other bioactive elements (e.g., Cd, Hg). Thus there is the potential for a wide range of synergistic and or antagonistic interactions among co-deposited species. Similar processes that affect these species may be important globally or in specific marine regions (e.g., nutrient nitrogen deposition to coastal regions).

#### **Important questions include:**

- \* How well do current models predict atmospheric deposition to the surface ocean?
- \* Will dust and iron source areas be wetter (i.e., more precipitation) or drier (i.e., more evaporation) in the coming century? How will land use, water use and higher levels of carbon dioxide affect desert dust sources?
- \* How will wind vectors in the mineral aerosol source regions change in the coming century and how will this affect the size distribution and resulting atmospheric residence times?
- \* How will the larger scale surface and upper air wind patterns change in the future and how will this affect the transport paths, deposition regions and deposition quantities of atmospheric dust?
- \* How will precipitation patterns over the ocean change and how will this influence the overall flux of dust to the ocean as well as the ratio of wet to dry deposition?
- \* Is the atmospheric deposition of nitrogen species increasing in open ocean regions downwind of rapidly growing population centers and agricultural regions?

#### ***B. What processes control the bioavailability of atmospherically supplied nutrients and bioactive elements?***

The bioavailability of atmospherically derived chemical compounds and elements in surface marine waters is dependent on three primary factors: 1) initial source chemical characterization, 2) atmospheric chemical processing and 3) seawater chemical and biological processing after deposition. The importance of each of

these factors is dependent on the chemical compound or element of interest. For example, some nutrient elements have gas phase precursors (e.g., N), others have high temperature combustion sources (e.g., Zn), and for others (e.g., Fe) soil dust itself is the source. We must first characterize the sources before we can determine what atmospheric chemical mechanisms may be important for changing the bioavailability of the chemical compound or element of interest.

One way to illustrate the various processes is to follow iron in mineral aerosols from terrestrial source regions to its deposition to surface waters. Dust properties could be significantly modified by interactions with other species during the transport (Gao and Anderson, 2001), consequently affecting aeolian Fe solubility and then its bioavailability. Therefore, iron bioavailability is an excellent example since it can potentially be affected by a complex array of processes. For example, the initial conditions may include: a fraction of iron present as iron-oxyhydroxide coatings compared to refractory forms of iron (e.g., iron bound in alumino-silicate minerals), the presence of complexing ligands that may promote solubilization of iron (e.g., oxalate), and the presence of chemical species that would influence the pH of the particle if incorporated into a cloudwater droplet (e.g., sulfuric and nitric acid). The refractory forms of iron should remain bound to the alumino-silicate matrix over the time scales of atmospheric transport, although the carrier mineral may change (e.g., clay mineral transformation). The iron-oxyhydroxides can undergo photo-reductive dissolution if the particles become incorporated into cloudwater droplets that contain photo-reactive organic compounds. These reductive dissolution mechanisms can lead to soluble ferrous iron (Fe(II)) which may result in more bioavailable forms of iron once deposited to surface sea waters.

The mass transfer mechanism (e.g., rain, dry deposition, haze/fog deposition) of iron between the atmosphere and the surface waters may also affect the bioavailability of iron after deposition. The examples cited above could result in a highly modified dust and subsequent dry deposition, or be amply represented in wet scavenging. Also the aqueous chemistry of seawater will have a major role on the bioavailability of atmospherically derived iron. Abiotic photochemical processes in the surface seawater can occur to enhance dissolved and available reduced forms that may be stabilized by complexation processes. Biotically, the production of chemical compounds by marine organisms (e.g., siderophores) can increase the soluble iron in seawater and thus may also influence the bioavailability of atmospherically derived iron. When iron exceeds solubility limits, it can form colloids; although these colloids are not directly bioavailable, they may serve as an iron redox reservoir that can be tapped when Fe inputs diminish (Wu et al., 2001), or for co-precipitated phosphate.

**Important questions include:**

- \* What are the timing and persistence of bioavailable inputs relative to the onset of biological demand?
- \* What is the photochemistry of the surface microlayer, in terms of chemical transformations and fluxes, including reflux back to the atmosphere or fluxes through the oceanic surface layer?
- \* To what extent is Fe released into seawater predetermined by photochemical reduction in atmospheric aerosols?
- \* Do complexing agents in seawater or actions by organisms (gut processes) increase the amount of iron available from refractory aerosols?
- \* To what extent is organically complexed Fe colloidal or truly soluble and how do these forms affect bioavailability of iron?
- \* What environmental factors control the solubility of aeolian iron in seawater?
- \* How does the input of bioavailable Fe scale with changes in mineral dust fluxes?

***C. How do nutrients derived from atmospheric sources affect marine biogeochemical processes and the relative availability of key limiting nutrients?***

A variety of atmospheric interactions can have direct bearing on the relative availability of nitrogen and phosphorus in surface waters. The P cycle largely relies on the input to the sea through weathering of phosphorus without any major connection to the atmosphere, although atmospheric inputs such as dust may affect dissolved inorganic P pools (see below). In contrast to P, the marine nitrogen cycle is closely linked to the atmosphere through the deposition of fixed N and by the processes of nitrogen fixation and denitrification which, respectively, provide primary input of fixed nitrogen from, and the loss of fixed N back to, the gaseous N<sub>2</sub> pool.

Atmospheric deposition of fixed nitrogen can directly affect the local N/P ratio and may be important in some regions. In nearshore and coastal regions, inorganic and organic N is deposited from the atmosphere to surface waters and can promote phytoplankton growth (e.g. Paerl, 1995; Paerl et al., 2001). Source strengths of atmospheric N deposition are expected to increase with future human population growth and the further development in coastal areas, as well as in open ocean regions downwind from major urban areas.

Perhaps the most intriguing effects of atmospheric processes on upper ocean biogeochemistry are through the transport of mineral aerosols from land to sea and the effects of these inputs (particularly iron) on several processes. Along with N and P, iron is also a critical nutrient required by all biological systems. We now recognize that large tracts of the world's ocean are characterized by high concentrations of nutrients and low concentrations of chlorophyll (HNLC regions); the biological productivity of these regions is different from that of the ocean at large in that they are limited by iron availability. Recent experiments have clearly demonstrated the strong influence of large-scale iron inputs through purposeful fertilization on plankton productivity in HNLC regions in the equatorial Pacific and the Southern Ocean (Martin et al. 1994; Coale et al. 1996; Boyd et al. 2000). Stimulation of DMS production was also observed in two of these experiments (Turner et al. 1996; Boyd et al. 2000). The primary natural source for iron in many of these ecosystems is through atmospheric deposition of aeolian dust.

Previous work has also shown atmospheric deposition in coastal regions to be enriched in both N and Fe and bioassay experiments have demonstrated potent stimulation of coastal and Gulf Stream productivity by N + Fe - the so called "Geritol Effect" (Paerl et al. 1999).

Iron also appears to be a critical factor in oligotrophic low nutrient low chlorophyll (LNLC) regions. While these regions are generally regarded as primarily nitrogen limited, there is accumulating geochemical and ecological evidence that N<sub>2</sub> fixation may be a key source of new nitrogen in these expansive ecosystems (Karl et al. 1997, Capone 2001). There is also strong circumstantial evidence that marine N<sub>2</sub> fixation in such areas may often be limited by availability of iron derived largely through the flux of aeolian dust (Gruber & Sarmiento 1997, Lenos et al. 2001). The extent of iron limitation of N<sub>2</sub> fixation may vary among ocean basins (Wu et al. 2000, Gao et al. 2001, Sanudo-Wilhelmy et al. 2001, Berman-Frank et al. 2001). Besides potentially affecting the N/P ratio of surface waters through stimulation of nitrogen fixation, aeolian dust fluxes to the surface ocean may also sorb and remove phosphate providing a further synergistic effect (with nitrogen fixation) on oceanic N/P (Krom et al. 1991).

Globally, N<sub>2</sub> fixation and denitrification need only balance on longer time scales (centuries to millennia); during key transitions, a temporary imbalance can alter oceanic N inventories. We hypothesize that during the inception of glacial periods, dust fluxes are high, N<sub>2</sub> fixation is enhanced and the ocean is slightly autotrophic and accumulates fixed N (i.e. global surface N/P ratios increase). Upon deglaciation, continental margins are flooded, providing major denitrifying zones absent during glacial periods, aeolian iron fluxes are relatively low, the ocean undergoes a net loss of fixed N and is slightly heterotrophic (i.e. global surface N/P ratios decrease) (Falkowski 1997). Areas of the contemporary ocean present sharp contrasts in the relative degree of iron limitation (Wu et al. 2001; Behrenfeld & Kolber 1999) and in extent of atmospheric Fe inputs (Fung et al. 2000; Gao et al. 2001) and thereby provide areas to both observationally and experimentally test these hypotheses.

The terrestrial physiography is changing, as anticipated, through shifts in climate and land use. The rate of change is expected to accelerate – along with the effects on the delivery of nutrients from land to sea, and, consequently, on the marine C and N cycles. In order to assess the sign and capacity of biologically mediated carbon fluxes, as well as the ocean's role in CFC production, in the coming decades and century, it is essential to understand the controlling processes and feedbacks with climate changes

**Important questions include:**

- \* How do atmospheric N inputs affect the structure and function of upper ocean ecosystems in nearshore regions subjected to substantial inputs of fixed N through the atmosphere?
- \* What are the response times of these populations to changes in atmospheric N inputs?
- \* Does the deposition of atmospheric nitrogen to the coastal environment have a deleterious impact?
- \* Does atmospherically derived N contribute to nuisance bloom formation in coastal waters?
- \* How do aeolian fluxes of Fe affect the structure and function of upper ocean ecosystems in the oligotrophic tropical and subtropical ocean?
- \* What are the response times of open ocean populations to iron inputs via dust deposition?
- \* Does Aeolian Fe deposition stimulate N<sub>2</sub> fixation? Where and how?
- \* Do aeolian iron inputs increase net CO<sub>2</sub> uptake and the fluxes of other CRCs?
- \* Are there synergistic responses to iron and nitrogen enrichment?
- \* How do such inputs affect CRC fluxes?
- \* Do aeolian dust fluxes provide sources of other important nutrients, and/or do they affect the availability of preexisting nutrients (e.g. phosphate) in biologically relevant ways?

**2. How do changes in biogeochemical processes in the surface ocean impact air/ sea exchange of CRCs? How do these processes feedback to radiative forcing?**

Four major biologically produced CRCs in the upper ocean are critical to understanding radiative forcing, namely, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and DMS. Of these, CO<sub>2</sub> has received the most attention. The direct and indirect effects of changes in atmospheric CO<sub>2</sub> on the formation of calcite by calcifying organisms, as well as upon opal formation by silicifying organisms, remains a major uncertainty in our projections of how functional groups of planktonic organisms will change in response to anthropogenic activities. On a molecular basis, however, both CH<sub>4</sub> and N<sub>2</sub>O have much greater (approximately 20 and 300 fold) greenhouse warming potentials than CO<sub>2</sub>, respectively.

The processes controlling the efflux of N<sub>2</sub>O and CH<sub>4</sub> from the ocean remain obscure. N<sub>2</sub>O can be formed from denitrification and nitrification (Capone 1996; Dore et al. 1998). The inventory of this gas appears to change markedly between glacial and interglacial conditions (Leuenberger & Siegenthaler 1992; Fluckiger et al. 1999), and it is essential to understand the underlying processes responsible for the changes and whether these processes will have positive or negative feedbacks on radiative forcing in the coming decades. Analysis of the isotopic composition of N<sub>2</sub>O preserved in ice cores may help reveal variations in the broad scale processes such as denitrification that contribute to its source.

Methane can also be produced in the upper water column. Shifts in climate, upper ocean fertility and anoxia can all potentially affect the flux of this greenhouse gas (Oremland 1979, Fuhrman & Capone 1991, Karl & Tilbrook 1994, Tilbrook & Karl 1995).

Field experiments in both the equatorial Pacific and Southern Ocean have shown the potential to increase DMS fluxes through iron enrichment (Turner et al. 1996; Boyd et al. 2000). However, while the potential feedback of DMS through cloud condensation nucleation and altered cloud albedo has been hypothesized for over a decade, there is no direct evidence that DMS fluxes are actually related to cloud albedo.

***A. What are the structures and processes in plankton communities that control the production and consumption of CRCs and their air/sea exchange?***

Production of CRCs such as DMS and halomethanes is correlated with total phytoplankton abundance, but a robust understanding of controls on the concentrations of these compounds and their exchanges with the atmosphere requires consideration of both the taxonomic composition of the phytoplankton and the dynamics of the entire plankton community. The exact processes involved in production and destruction of these compounds are in many cases still unknown, and oceanic sinks may be significant even for compounds for which the ocean is a net source. The dynamic balance between production and consumption in the surface ocean is therefore critical to understanding the controls on atmosphere-ocean exchange. It is first necessary to understand what the processes are that result in the production of these compounds.

Important questions include:

- \* Is the critical step simply production by phytoplankton and consumption by bacteria, or is it bacterial modification of some precursor compound (such as DMSP)?
- \* If both pathways exist, what is the balance between them and how is it regulated?
- \* If the compound is produced directly by autotrophs, is the rate of production primarily a function of biomass, photosynthetic production, or other factors such as nutrient or osmotic stress?
- \* If bacteria play a significant role, how diverse are the bacteria responsible, and what regulates their abundance?

***B. What are the feedbacks from ocean biogeochemistry to climate and how do these feedbacks interact?***

There may be important feedbacks between atmospheric fluxes of nutrients into the upper ocean and the flux back to the atmosphere of CRCs produced by the upper ocean pelagic food web. Numerous possible scenarios for feedbacks have been hypothesized. As we explore the biogeochemical dynamics of the upper ocean, many more possibilities become apparent.

For example, phytoplankton in HNLC regions, stimulated by iron from aeolian sources, could consume additional CO<sub>2</sub> and effectively remove it from the surface layer by transport to deeper waters. (However neither IronExII nor SOIREE observed increased particulate organic export: Coale et al. 1996; Boyd et al. 2000). This could result in increased flux of CO<sub>2</sub> from the atmosphere that could contribute to a negative climate feedback. Furthermore, increased production of dimethyl sulfide (DMS) in the surface layer also occurs via phytoplankton and its associated food web and has been observed in two Fe enrichment experiments (Turner et al. 1996; Boyd et al. 2000). Enhanced DMS flux into the atmosphere, followed by oxidation to sulfate aerosols, could increase albedo, again contributing to cooling. Enhanced flux of organic C could also promote hypoxia in subeuphotic zone waters with attendant increases in the production of N<sub>2</sub>O and CH<sub>4</sub> (Fuhrman & Capone 1991).

As suggested above (Section I.A), another feedback scenario among aeolian iron inputs, N<sub>2</sub>-fixing cyanobacteria, and climate may occur in low nitrate low chlorophyll (LNLC) regions. If the flux of dust and its associated iron to LNLC regions increases during warming periods, stimulation of N<sub>2</sub> fixation could provide a negative, stabilizing feedback to climate through the enhanced uptake and sequestration of atmospheric CO<sub>2</sub>. The enhanced growth might have similar, but less rapid, consequences as the first scenario. This latter scenario would also require either a source of phosphorus relative to new nitrogen derived from N<sub>2</sub> fixation or higher export ratios of C:P and N:P (i.e. lower export of P).

Alternatively, decreased dust flux to either HNLC or LNLC regions during warming periods would restrict or decrease upper water column primary productivity, or N<sub>2</sub> fixation and any C sequestration associated with it, thereby leading to greater efflux of CO<sub>2</sub> from these regions and a positive feedback to warming.

Feedbacks to climate will also directly affect dust production, increasing the level of complexity in the interactions. The intensity and impact of dust inputs may differ across latitude and among ocean basins. One can also envision possible effects resulting from dust including the input of other nutrients that can limit phytoplankton growth (i.e. nitrogen, manganese, silicate) or the sorption and removal of nutrients such as phosphate. The direct feedback to the atmosphere resulting from changed productivity may not be the most important mechanism for affecting climate. Changes in phytoplankton and food web structure (e.g. diatoms over prymnesiophytes or cyanobacteria) could lead to dramatic changes in the quality, composition, and quantity of material emitted across the air-sea interface or exported to the ocean interior.

The first challenge is to detail and document important feedbacks. Even more daunting is the task of elucidating multiple feedback mechanisms between the upper ocean and atmosphere. Nonetheless knowledge about these processes is critical to advancing our understanding of these systems and to developing a predictive capability.

Important questions include:

- \* What are the important positive and negative feedbacks to climate arising from the interaction between atmospheric nutrient inputs and upper ocean biogeochemistry and biology?
- \* What are the response times of these feedbacks?
- \* How do multiple feedbacks interact?

***C. How important is the sea surface microlayer, what controls its formation and composition, and what role does it play in air/sea exchange?***

The sea surface microlayer is a unique microenvironment that serves as the boundary layer between ocean and atmosphere (Liss & Duce, 1997). The microlayer can serve to damp capillary waves that influence the turbulence of the ocean surface and thus the air-sea transfer of aerosols and gases. The thickness and composition of the microlayer determines the extent of this influence. Both physical thickness and chemical composition depend on physical processes (e.g., temperature, wind velocity) and biological processes (e.g., biological production and consumption of POC and DOC) that change seasonally and may change on longer time scales. Due to the high concentrations of many dissolved and particulate materials as well as microorganisms directly at the air/sea interface, the sea surface microlayer is particularly susceptible to photochemical reactions and interactions that may lead to trace gas production/destruction and conversion between the dissolved and particulate phases. Although much is known about microlayers, particularly about their formation mechanisms, we have insufficient knowledge of their chemical composition, their role in the production of sea salt aerosols, their geographical extent, their photochemical interactions, the amount of coverage to predict how they will influence ocean turbulence on larger spatial and temporal scales, and how this influence will be affected by anthropogenic change.

Condensed organic material, such as that found in the sea surface microlayer and on the surface of oceanic bubbles, is one of the least-understood components of marine aerosols, even though it may have a dramatic



effect on hygroscopic growth and cloud nucleating properties (Jacobsen *et al.*, 2000). Much of the organic material processed through the marine boundary layer is emitted from the ocean to the atmosphere in association with sea-salt aerosols by concentration from bulk seawater onto the walls of bubbles and subsequent ejection into the atmosphere upon bubble bursting. Organics associated with sea salt react in the aqueous phase to produce both volatile and particulate products (Kawamura *et al.*, 1996). Other sources of condensed organic material include primary processes that release biological aerosols (e.g., bacteria and cell fragments) through the sea surface microlayer to the atmosphere. Identification of these organic compounds in the sea surface microlayer has been impeded both by sampling artifacts and by the large number of compounds and ill-defined humic substances that are involved.

Important questions include:

- \* What are the chemical constituents of the sea surface organic microlayer and how can the microlayer be accurately sampled?
- \* Is the chemistry of the surface microlayer relatively uniform or highly variable? What are the relevant scales of variability?
- \* What is the impact of the surface microlayer on the organic composition and physical properties of the sea salt aerosol?
- \* What are the effects of the surface microlayer on wind-wave interactions and gas exchange?
- \* Do aerosol organics derived from the microlayer specifically contribute to CCN?

***D. What controls near-surface phytoplankton accumulations, what feedbacks do these accumulations have on the oceanic boundary layer and are they important***

Many species of phytoplankton are known to discolor surface oceanic waters and cause “red tides”, “green” tides, “brown” tides, etc. Some of these phytoplankton are very important because of the role they may play in environmental or climate change; others have important societal relevance through direct health and/ or economic impact. While these phenomena are often due to a rapid growth of populations, high concentration of cells at the very surface could also be a response to changes in surface physical forcing such as reduced wind speeds and wave action. Surface plankton accumulations will have a very different impact on the exchange of material across the air/sea interface than blooms of phytoplankton that occur through the mixed layer.

We must understand what controls these near surface accumulations and the physical and biogeochemical feedback of these surface blooms – their causes and consequences in the boundary layer. For example, some blooms may result from episodic atmospheric delivery of nutrients. Decaying blooms often release gases including CRCs back to the atmosphere. We need to know what phytoplankton species form near surface accumulations and why they do they do it. The physical and chemical forcing that impact these species should be examined as well as the feedbacks to the boundary layer such as 1) changes in heat content of the surface layer, 2) changes in spectral quality and quantity of the *in-situ* light field, 3) changes in surface tension, gas exchange, etc., through the air sea interface, 4) changes in the boundary layer food web dynamics through changes in surface nutrients. These surface phenomena are very patchy in time and space and do not have a normal mode distribution. However, we do not know if they have hurricane-like impacts – i.e., although they are episodic in time and space, their impact integrated over long time scales is more profound than the mean condition. There is also a perception that harmful algal blooms (HABs) are becoming more common and are somehow related to anthropogenic activity. With respect to HABs, the atmosphere can serve as the conduit for transport of noxious or toxic aerosols generated in blooms.

Understanding these issues will help us determine whether climate and environmental change is producing more of these blooms in coastal oceans and what their consequences are.

**Important questions include:**

- \* Does a near-surface bloom of *Phaeocystis* release more DMS to the atmosphere than a bloom through the mixed layer?
- \* Is the effect of calcification by near-surface Coccolithophore blooms on the oceanic carbon cycle different from that of a mixed layer bloom?
- \* What is the fate of nitrogen released by a surface *Trichodesmium* bloom?
- \* Do surface accumulations of *Trichodesmium* contribute significantly to dinitrogen fixation?
- \* Are these blooms an important source of CRC's?
- \* How are noxious or toxic aerosols generated and transported from blooms?

***E. Is there information in the paleo record that can document how marine biogeochemical processes have changed in the past and explain responses to changing climate? What do we need to derive robust interpretations of these data?***

Ocean processes that regulate the production and consumption of CRCs are also sensitive to climate change, but the sensitivity of these processes to climate change has received little study and only over a limited range of climate variability. Instrumental records of relevant climate parameters extend back for only a limited time. Paleo-proxies are needed to develop a more complete picture of the response of the physical and biogeochemical state of the surface ocean to changes in atmospheric forcing. Micropaleontological and geochemical tracers preserved in sediments provide records of past changes in ecosystem structure, biogeochemical cycles, and environmental parameters. Reading these records accurately is made difficult, however, because the formation, preservation and burial of each proxy are influenced by multiple processes and factors. Consequently, it is rarely possible to linearly scale a proxy record extracted from sediments to the parameter of interest in surface waters.

In order to develop more reliable reconstructions of past variability in surface layer parameters, and their sensitivity to climate change, it is essential that we understand more completely the processes influencing the formation, preservation and burial of proxies. These processes are best examined within the context of large interdisciplinary studies where a wealth of complementary information generated by the mainstream efforts is available to interpret the factors influencing the proxy records. Proxy development in the context of larger studies is cost effective, in that the complex array of interactions between proxies and processes can be examined at little additional cost. Often such studies will not add to the cost to the program per se, as funding can often be obtained from other sources to support proxy development.

SOLAS, in return for building into its research agenda the development of paleo-proxies, is benefited by the improved interpretation of proxy records. This capability will provide a basis for understanding sensitivities within the system to changes that have not occurred within the instrumental records, but which have occurred in the past and might occur in the future. Proxy records can be used to test the robustness of models by running them under boundary conditions that differ from those of today

**Important questions include:**

- \* Are proxies for sea surface temperature (e.g., alkenone Uk37 and foraminiferal  $d^{18}O$ ) sensitive to changes in environmental parameters and ecosystem structure?
- \* Are proxies for carbon export (flux; e.g., excess barium) sensitive to changes in environmental parameters and ecosystem structure?
- \* Can mixed layer depth be reconstructed from the relative abundance of different species whose microfossils are preserved in sediments?
- \* Can the stratification of the upper thermocline (density gradient) be reconstructed from the relative abundance of different species whose microfossils are preserved in sediments?
- \* Can each of the factors influencing the carbon isotopic composition of organic matter be constrained well enough to reconstruct surface  $pCO_2$  from the carbon isotopic composition of sedimentary organic matter?
- \* Can proxies (e.g., organic biomarkers) be developed to reconstruct past changes in the production of DMS and other CRCs?
- \* Can proxies of physiological state (growth rate) be developed to reconstruct past changes in iron sufficiency?
- \* Can trends in major biogeochemical processes such as  $N_2$  fixation and/ or denitrification be extracted from the paleo record?
- \* How can we separate utilization efficiency changes, water mass variability, and whole-ocean N isotope ratio changes as we interpret N isotope records from paleoclimatic archives?
- \* Can we improve our knowledge of the phasing of past atmospheric  $CO_2$  changes relative to other changes (sea level, dust fluxes) to better assess our hypotheses for glacial  $CO_2$  cycles?
- \* Can we better understand the relationship between total dust flux and solubilized iron (variable solubilization) to make improved models of the relationship between past dust fluxes and the availability of iron in the ocean?

**VII. 3 IMPLEMENTATION OF SCIENCE GOALS**

[To be developed]

**VII. 4 EXAMPLES OF HIGH PROFILE PROJECTS TO REACH GOALS****1. Natural Iron Fertilization:**

Aeolian Fe input to the ocean through both wet (by precipitation scavenging) and dry deposition represent natural iron fertilization events that can be used to understand the role of iron as a critical nutrient in many areas of the ocean. The incorporation of mineral dust and its Fe in precipitation (and incorporation in clouds) may increase the Fe solubility and its bioavailability to phytoplankton in the surface ocean, as mentioned earlier (Kieber et al. 2001). The biological uptake of Fe largely depends on its solubility and chemical speciation in seawater (Wells et al. 1995). Photochemical reactions in more acidic cloud waters and precipitation may promote dissolution of Fe in dust, and thus the input of Fe by precipitation may be

particularly important. A study conducted in the oligotrophic eastern Mediterranean shows a clear positive correlation between Chl *a* concentrations in the surface waters and precipitation rates (Ziveri et al. 2000), suggesting that aeolian Fe input through precipitation washout may result in more Fe that can be readily used by marine organisms. Recent modeling results through partitioning of the two deposition processes (dry + wet) suggest that wet deposition through precipitation scavenging accounts for ~40% of the total Fe deposition over the coastal sea and ~60% over the open ocean (Gao et al. 2001). The important role of wet iron deposition is confirmed in studies off Bermuda, where such a wet flux during summer stratification resulted in apparent new production from N<sub>2</sub> fixation (Kim & Church 2001, in press). Thus episodic precipitation events, as well as larger scale precipitation systems, may serve as natural Fe fertilization experiments that can be used to understand the responses of phytoplankton and other organisms. Three different types of natural Fe fertilization experiments are suggested.

#### ***A. Barbados Dust Deposition Experiment: BarDEx***

There is a high priority to characterize wet (and total) removal processes in regions where dust concentrations are known to be high. An experiment is proposed to take place in the tropical North Atlantic in the region of Barbados where trade winds carry high concentrations of dust during late spring, summer and early fall (Prospero & Nees, 1986). This experiment would have three objectives:

- 1) To characterize the removal rates of mineral dust and related aerosol particles in rain events.
- 2) To measure the deposition rate of dust to the ocean surface in individual rain events and to follow the subsequent changes in the concentration of Fe and other species in the surface waters.
- 3) To document biological and biogeochemical responses to these inputs

The program would include the following components:

- a) A land-based study of mineral particles in the aerosol and precipitation phases would include measurement of full size distributions (including super-large particles using a rotary impactor) and size/composition. Precipitation studies would use Coulter counter measurement of size distributions. The removal rates in individual rain events would be related to aerosol concentrations based on vertical profile measurements. The composition (Fe and other species) of the aerosols/dust/precipitation samples would be measured. Many of these measurements are needed in order to relate the dust studies to remote-sensing products that will be used to generalize the results to larger regions.
- b) A ship-based study of dust deposition rates and Fe/Al dissolution amounts could use a relatively small vessel to follow individual cumulus cloud rain events and to measure dust concentrations in the deposition region. The rain events would be tracked with a coastal based radar and/or radar on the ship, providing information on aerosol-cloud interactions of individual cumulus elements. Rain deposition areas would be identified based on the greater hydrogen peroxide concentrations in rainwater. This can be mapped in surface seawater using an in situ peroxide detector. The rain mixing depth would be determined by profiling the peroxide distribution. Simultaneously the Fe and Al distribution would be mapped using reliable in situ detection systems. Periodic grab samples would be collected to make high-precision dissolved and particulate Fe and Al measurements. With typical dissolved Fe concentrations in rain of about 100 nM on Barbados, a rain event of 1 cm and a short term rain mixing depth of 1 m would result in an increased seawater dissolved Fe concentration of ~1 nM, which is likely a lower limit. Typical detection limits for Fe are ~0.1 nM.

Simple, underway determination of surface chlorophyll and fast repetition rate (FRR) fluorimetry would be used to determine short-term biological responses to these inputs and would be coupled to ocean color (e.g. SeaWiFS, MODIS) observations. Depending on preliminary results, more detailed biogeochemical studies involving characterization of key phytoplankton (e.g. diazotrophs), their response over time to inputs, effects on primary production and N<sub>2</sub> fixation, and dynamics in inorganic nutrient and CRC pools would be undertaken. An appropriately located mooring (similar to the Bermuda Testbed Mooring with physical, bio-optical, and chemical sensing/sampling devices), would be a valuable addition to the experiment.

c) Measurement of the vertical distribution of aerosols. This is necessary to develop a better understanding of surface deposition rates in terms of meteorological conditions and to relate the measurements to various satellite sensors. Vertical distributions could be obtained with a micropulse lidar and by inferring a column loading based on aerosol optical thickness using AERONET data from the island.

d) Mapping the dust concentration fields using the TOMS absorbing aerosol product. It has been shown to give excellent results relative to ground-based measurements.

e) Modeling of dust removal rates to the ocean. Many dust-modeling groups are eager to address the issue, and close cooperation is expected. Some models do remarkably well in characterizing the long-term record at Barbados. Predictive models would be extremely useful in anticipating dust/rain events for planning purposes.

f) Provenance studies to determine sources of desert dust (similar to Biscaye et al., 1997). This will assist in determining whether land use practices or water use practices are affecting dust deposition.

### ***B. Tracking Tropical Eddies***

It is necessary to study the effects of Fe deposition into present-day high nutrient waters in order to understand the biogeochemical response of HNLC regions to past changes in dust deposition rates and to anticipate future changes. In addition to deliberate fertilization experiments using shipboard seeding of limited regions, the role that atmospheric Fe deposition plays in modifying surface water biogeochemical processes can be investigated directly by utilizing natural surface water Fe fertilizations. These Fe addition experiments occur naturally in the tropical Atlantic where upwelling of high nutrient water along the West African coasts leads to eddies that are advected into the equatorial current system (Vink and Measures, 2001). The proximity of the Saharan dust source to the advective path of these eddies ensures that sufficient Fe is added to these initially low-Fe high-nutrient waters to permit full utilization of the upwelled nutrients.

A successful program would require many of the same elements outlined in the BarDEx project above, in fact the goals of these two projects might be combined in the same expedition.

Land-based characterization of the atmospheric source term would include particle size distribution and chemical composition. Synergistic modeling efforts aimed at predicting deposition would use satellite data of regional coverage e.g. TOMS as well as vertical distribution data obtained from LIDAR.

Shipboard work would involve initial biological and biogeochemical characterization of the eddies and tagging them with transmitting isopycnal floats, and a chemical tracer such as SF<sub>6</sub> as they form off the coast of NW Africa. The eddies would then be tracked using satellite and the features revisited to follow their biogeochemical evolution. It is envisaged that several eddies would be tagged and followed with the ship visiting each in turn to observe the progression of the Fe fertilization.

The shipboard biogeochemical work would consist of many of the same parameters outlined in VII.4.1A above, (dissolved and particulate Fe and Al to locate and quantify mineral deposition; hydrogen peroxide to locate precipitation events, and FRRF and Chl a to monitor photosynthetic biological responses. In addition shipboard work (which will require a larger vessel than BarDex) should lead to estimates of the changes in the biological food web. In particular this would involve specific experiments designed to assess the role of grazing pressure and how it changes after an input event. This work should be linked to the shipboard determination of the production of CRR gases such as DMS to allow quantification of the role that food web dynamics plays in CRR production.

In quantifying the biological response of such systems to natural atmospheric inputs and determining their effect on ocean-atmosphere gas fluxes we obtain essential data for ground-truthing models that seek to predict ocean-atmosphere responses to changes in dust fluxes.

(The region north out of Barbados could cover the trade wind shower experiment proposed separately. The same expedition could also sample eddies transiting the ITCZ from the east, also proposed separately below.)

### ***C. Experiments Using Transects of the ITCZ***

The Saharan dust plume is carried by the easterly Trades both north and south of the Atlantic equator to be entrained in the ITCZ (Inter-Tropical Convergence Zone). The ITCZ upwells humid air causing extensive and continual precipitation leading to the scavenging of Saharan dust. An oceanographic expedition is proposed to transit the ITCZ to study the natural processes of atmospheric weathering of the dust and consequential release to surface seawater. One should observe the response of oceanic biota to iron release, for example by determining trends in chlorophyll, shifts in phytoplankton speciation and relevant processes such as primary productivity and N<sub>2</sub> fixation. One can also mimic such observations by taking collections of aeolian dust and introducing them to on-deck incubations with measurements of the concentrations of iron and nitrogen species. The surrounding areas north and south could be used to study the different effects of dry vs. wet fallout characteristic of the ITCZ.

The Indian Ocean is another ideal location to study the effect of nutrient deposition from the atmosphere on surface ocean biogeochemistry. The equatorial Indian Ocean is less complex physically (e.g. eddies, major riverine influences such as the Amazon and Congo rivers) and is therefore less complex biogeochemically than the Atlantic Ocean. It receives inputs of dust from the Arabian desert and disturbed soils of south Asia, as well as the anthropogenic aerosol pollutants from the Indian Subcontinent. The ITCZ of the Indian Ocean serves as a “curtain” separating the impacted northern equatorial from the more pristine south equatorial waters. The INDOEX field campaign characterized the atmospheric input into the region and these results can be used to plan a SOLAS experiment that would study the effect of this input on the surface ocean.

## **2. Iron Fertilization in LNLC Areas**

Several open-ocean direct-Fe-enrichment experiments have been undertaken in HNLC regions. These studies have provided definitive evidence of the important role of iron as a key controlling nutrient in the equatorial Pacific and Southern Oceans (Coale et al. 1996; Boyd et al 2000). It is also hypothesized that iron may be a key factor in LNLC regions through its influence on N<sub>2</sub> fixation (Falkowski 1997). ***An open ocean iron fertilization experiment in an LNLC region to test the effect of iron on open ocean populations would be a quintessential SOLAS activity.***

Areas of the world's oceans with evidence of high levels of nitrogen fixation (e.g. as inferred by large positive N\* anomalies) are also areas that receive substantial atmospheric inputs of dust (Gruber & Sarmiento 1997; see Capone 2001, Berman-Frank et al. 2001). Recent evidence suggests that in fact, diazotrophic populations of the tropical Atlantic may often be iron sufficient (Wu et al. 2000; Sanudo-Wilhelmy 2001). In contrast, areas of the southwest Pacific are far removed from continental dust sources and phytoplankton populations there appear to be severely iron limited (Behrenfeld & Kolber 1999). The southwest Pacific, which also harbors populations of *Trichodesmium* and other diazotrophs (Dupouy et al. 2000), may be the most appropriate area to examine experimentally and on a mesoscale, the connection between iron inputs and upper ocean N<sub>2</sub> fixation.

Given the relatively slow growth rates of the predominant diazotroph, *Trichodesmium*, the approach taken may need to be fundamentally different than that used in HNLC regions. Longer term fertilization, for example by development of a sustained iron plume for multiple weeks, may be required to elicit a response by the diazotrophic component. A site would need to be carefully chosen with respect to its physical dynamics and logistical feasibility.

A combination of coupled ship, land and satellite-based studies would be most appropriate. Field efforts in the plume would include examination of both diazotrophic (including non-*Trichodesmium* sources) and non-diazotrophic plankton population response (compositional, physiological [e.g. FRR fluorometry, primary productivity and N<sub>2</sub> fixation] and biogeochemical [e.g. pCO<sub>2</sub>, nutrient and  $\delta^{15}\text{N}$  fields]). Ideally, concurrent examination of CO<sub>2</sub> dynamics and other CRCs would be conducted.

### 3. Experiments Evaluating Effects of Coastal Atmospheric N Deposition?

Atmospheric inputs of new N, associated with expanding human use and development of coastal watersheds and airsheds are increasing (Vitousek et al., 1997, Paerl et al., 2000). It has been estimated that ~10 to >40% of new N inputs into coastal waters are now of atmospheric origin (Paerl et al 2000), much of it attributable to growing agricultural, urban and industrial emissions (Martin et al. 1989, Duce et al. 1991, Paerl 1995, Valigura et al., 2000). This represents at least a ten-fold increase in atmospheric N emissions over pre-industrial and Agricultural Revolution (early 1800s) (Howarth et al., 1996; Holland et al., 1999). In North America, coastal AD-N ranges from 400 to over 1000 mgN m<sup>-2</sup> y<sup>-1</sup>, while in the highly urbanized, industrialized and intensively-farmed regions of Western Europe deposition commonly exceeds 1 gN m<sup>-2</sup> y<sup>-1</sup> (Prospero et al., 1996; Holland et al., 1999). The relative contribution of AD-N to coastal N budgets is expected to increase substantially in the early part of the next century (Galloway et al., 1994), when nearly 70% of the US and European populations will reside within 50 km of the coast. On regional and global scales, AD-N constitutes a significant input of new N to the oceanic environment; accounting for ~40 TgN y<sup>-1</sup>.

There is an urgent need to directly examine the trophic (productivity, food web structure and function) and biogeochemical (C, N and other nutrient fluxes) impacts of atmospherically-deposited N (AD-N) in coastal and off-shore waters. Several studies have now shown that at naturally-occurring deposition rates, AD-N can enhance primary productivity and phytoplankton biomass in a variety of coastal ecosystems (Paerl et al, 2000). Similar studies need to be initiated in off-shore and open ocean waters now known to be impacted by ever-increasing rates of AD-N (Galloway et al., 1994), especially reduced forms (ammonium, organic N) (Paerl et al., 2000, Cornell et al., 2001). In particular, potential links between AD-N, and troublesome symptoms of advanced eutrophication (hypoxia, harmful algal blooms) must be examined and evaluated using an array of micro- and mesoscale bioassay experiments incubated under natural irradiance and temperature conditions. These experiments can be coupled to emerging biochemical and molecular techniques capable of identifying and characterizing specific microbial (algal and bacterial) and higher taxa indicative of water quality, trophic state and habitat conditions. This need is particularly acute in coastal waters downwind of developing regions, such as mainland Asia (China), Africa, and South America. Some specific issues and phenomena requiring experimental evaluation include:

- 1) Event-scale biological response (bioassay) experiments over a range of AD-N input/loading scenarios (i.e., episodic storm events vs. chronic (dry deposition) loading events).
- 2) Seasonal studies that would examine the impacts of AD-N and Fe on different phytoplankton communities.
- 3) Impacts of dry vs. wet deposition on productivity and community structure.
- 4) Impacts over a range of locations going from highly impacted estuaries to pristine oligotrophic waters (e.g., Neuse-Pamlico to Sargasso Sea along mid-Atlantic region).
- 5) Couple response bioassays to depositional models (i.e., along the mid-Atlantic this could be done by coupling experimental work to the Extended Regional Acid Deposition Model (RADM)).
- 6) Examine N-Fe synergism among naturally occurring phytoplankton communities, using either shore-situated or ship board bioassays.

All the above should be examined over a geographic range of locations on a seasonal basis.

### **III. Basic Needs for the Program ("housekeeping items")**

**[To be intertwined with input from the other groups]**

#### **I. Role of Time Series**

The atmospheric input of biogeochemically relevant trace elements (e.g. limiting new nutrients) to the surface ocean is transient in time and space. Emissions from source regions can vary according to climate (e.g. drought in arid regions), changes in meteorology and climate that effect wind fields (e.g. ENSO, NAO), changes in regional economies (e.g., rapid industrialization in Asia), and emission controls (e.g. Clean Air Act). The time scale of these changes in the atmospheric delivery and the oceanic response can be long (decades). Consequently there is a need for continuous time series records at key marine locations.

Progress on SOLAS objectives requires supporting data that places individual studies in context. For example, we will need to know whether a SOLAS process study on oceanic biogeochemical responses to dust input was undertaken at a time when dust input was at normal levels or if dust conditions were anomalous. Such data can only be obtained from long-term time series measurements made at strategically-located ocean stations. Gaps in time series make it more difficult to interpret data. The importance of these time series is illustrated by Charles Keeling's Mauna Loa CO<sub>2</sub> record, one of the lynchpins of our understanding of the global carbon cycle and the perturbations caused by humans.. The threats of discontinuity are equally well illustrated by that time series: NSF funding for that effort was cut off for awhile after the first few years, and it was continued without gaps only through the wisdom of Roger Revelle and his powers as director of the Scripps Institution of Oceanography.

Some important ocean time series stations are presently in place (e.g. Bermuda Atlantic Time Series [BATS], Hawaii Ocean Time-series [HOT], Palmer) where long term data records have been established for key biological, chemical and physical parameters. However, their continuity has been broken and is continually threatened because of hiatuses in programs or lack of funding to maintain platforms. Regrettably, some important time series have now been discontinued (e.g. the high frequency AEROCE dust time series at Bermuda) or interrupted (e.g. the HALE/ALOHA biogeochemical mooring off Hawaii). Other time series are maintained from one short-term grant to the next with no assurance of continuity (e.g., the Bermuda Testbed Mooring). Physical maintenance of infrastructure is often neglected (e.g. atmospheric sampling towers in Bermuda and Hawaii), and in some cases, their continued existence is threatened by competition for space. For example, if the Bermuda AEROCE sampling tower is neglected and removed, it could never be reconstructed because of new zoning regulations.

SOLAS should also make maximum use of present and planned fixed moorings as well as drifting ocean observation platforms. In the equatorial Pacific Ocean, the TOGA/TAO array of moorings have already provided invaluable information on surface ocean/atmosphere interactions. Similarly, the PIRATA moorings in the equatorial Atlantic ocean could be used to study atmospheric and oceanic fluxes of material as proposed in the sections above. SOLAS should work in concert with programs such as CLIVAR to outfit these moorings with appropriate sensors to provide high resolution time series in-situ measurements of parameters such as phytoplankton concentration, iron flux etc.

We should also take advantage of coastal locations in nutrient (N)-sensitive regions downwind of significant emission sources. Some of these are already in place though local monitoring programs (i.e., URI/ Narragansett, Coastal Delaware, UNC-CH/IMS/Coastal NC). However, they need to be formally incorporated into collaborative long-term monitoring and assessment efforts.

Our community recognizes the importance of continuing these time series, but the structure of our system of science funding requires vigilance to prevent their loss. One of the most important and cost-effective achievements of the early phases of SOLAS would be to restore and bolster important long-term time series. A continuing goal of a mature SOLAS should be to foster these time series, ensure their maintenance during the lifetime of SOLAS, and pave the way for a transition to their continuation in future



projects. Thus one of the first order priorities for US-SOLAS is to guarantee the support to continue these time series and establish others in key locations.

Key data in the atmosphere include basic meteorological parameters such as solar radiation, wind, precipitation, and aerosol composition. These allow identification of important events that could affect forcing and exchange at the air-sea interface. Key data in the water also include radiation properties, temperature, salinity, nutrients, productivity, and species composition. This would allow one to track gradual changes in ecosystem responding to transients in atmospheric delivery. With the development of new technologies, data at the sea surface could include sea spray and bubble spectra, or surface tension. The protocol should also include measurements that would permit the integration of *in situ* data with remotely sensed properties. For example, ground-based measurements of spectral aerosol optical depth can be used to calibrate on a regional basis satellite-derived aerosol products; the satellite measurement can then be used to map out regional aerosol distributions with increased confidence in the quality of the data.

The atmosphere and ocean time series measurements should be co-located and synoptic. Stations should be established on or near oceanic islands to facilitate logistics and maintenance of instruments on atmospheric towers or hydrographic stations. Where there are no islands, buoys could be used for both physical and chemical sampling.

Low frequency time series over large spatial regions will be vital to understanding global scale shifts in atmospheric-ocean interactions that occur on decadal scales as a result of natural climatic and anthropogenic forcing functions. The integrating power of the surface ocean when combined with proxy tracers of atmospheric deposition can be exploited to investigate large-scale low frequency shifts in deposition patterns.

A transect through the Atlantic Ocean, for example, would sample regions where dust fluxes range from  $\sim 0.1$  to  $>10$  g mineral dust  $\text{m}^{-2} \text{yr}^{-1}$ . By combining measurements of a geochemical proxy of dust deposition (Al) (Measures and Vink, 2000) with determinations of Fe, N, P, and biological parameters such as FRRF etc., the relationship between the atmospheric forcing function (deposition), the geochemical transfer function (surface water chemistry) and biological responses can be investigated under a wide range of deposition conditions. The determination of additional parameters such as DMS and other CRC production and other parameters relevant to SOLAS goals would provide important insights into the relationships between the entire suites of variables. Repeating this section at annual intervals would provide a baseline for estimating changes in the pattern and magnitude of atmospheric deposition and thus allow a direct estimate of the concomitant changes in surface water biogeochemical processes in response to natural climatic change processes. These results could then be used to refine and improve the modeling approaches to oceanic dust and iron deposition and their effects on the biogeochemical coupling between the surface ocean and the atmosphere.

## **II. Integration of Modeling in SOLAS**

Models of climate impacts must incorporate a series of complex processes starting with emissions, transport, deposition to the oceans, and ending with the chemical and biological responses in the oceans.

Chemical transport models (GTMs) have improved greatly over the past decade. Recent intercomparisons of GTMs (including those in the recent IPCC assessment) show that they can do an excellent job with many anthropogenic emissions (e.g., SO<sub>x</sub>-sulfate, CO). The GTMs worst performance was with dust. Dust generation is a highly non-linear process that depends on many factors including soil composition, soil moisture, the conditions of the soil surface (e.g., the types and coverage of vegetation, if any; the degree to which the soil surface is disturbed), and local wind fields. Some models require a considerable knowledge of soil properties; unfortunately such information is unavailable for vast regions of the earth including some that contain the most intense dust sources. The second major problem in modeling dust is the parameterization of the removal process. Estimation of dry deposition requires a good knowledge of particle size distributions, a property that models do not handle well. As for wet deposition, the combination of the large temporal variability of dust concentrations and the sporadic nature of rainfall

makes it difficult to model this process. Despite these problems some models have done a reasonably good job of characterizing dust transport from specific regions (e.g., North Africa to the tropical North Atlantic) by “tuning” the models. Unfortunately, when such models are applied on a global basis, the performance is very poor; for example, most models suggest that Australia is a dust source that is comparable in strength to North Africa when, in fact, very little dust is carried out of Australia. Until we have models that do a credible job with present-day dust transport, we cannot begin to assess the possible impact of climate change in the future.

SOLAS can contribute to the development of models by providing measurements of aerosol properties in the ocean receptor areas. These include measurements of particle concentration, size, and composition in the atmosphere and in precipitation. The concentration and size measurements will assist in the physical development of the model and the dust composition in developing genetic relationships to the soils in the source regions.

Modeling production of CRCs in the surface ocean requires improved understanding of the response of plankton communities to nutrient and atmospheric forcing. CRC production rates depend on the taxonomic composition of the phytoplankton, and models of the evolution of species in communities are still very uncertain. The concentration of CRCs is, furthermore, a function not only of the types of phytoplankton present, but of dynamical processes involving the entire plankton community. Models of these processes need to be developed, tested, and validated. There are no models currently in the literature that can be reliably utilized “off the shelf”. The abiotic chemistry of trace elements such as Fe, and their interactions with major elements such as P, is also represented poorly, if at all, in current models. All of these models need to be embedded in the best available models of ocean circulation, stratification, and mixing. Greater understanding of meteorological forcing of biogeochemistry as well as of biogeochemical processes themselves is necessary before reliable scenarios of the response of plankton community dynamics and associated CRC fluxes to climate variability can be generated.

### **III. SOLAS-Specific Remote Sensing Needs**

Satellite data will play an important role in attaining SOLAS objectives. As previously stated, remotely-sensed measurements provide critically needed information on the temporal and spatial variability of aerosols which would otherwise not be available. In the oceans, the oft-referred to limitation of poor depth penetration of remotely-sensed measurements is less of a drawback when emphasizing the atmosphere-ocean interface and oceanic boundary layer. Though incomplete in terms of variables measured (for a list see the international SOLAS Science Plan), they are invaluable when linked with concurrent field programs and modeling approaches.

It is extraordinarily important that emphasis be placed on satellite observations concurrently with field programs from the onset. The contribution that satellites can provide are:

- the best possible coverage in space and time, thus enabling extrapolation of point or line measurements to larger scales
- a context for oceanographic processes both in space and time (e.g. presence of eddies or plumes, shifts in wind direction) which can lead to improved understanding of the underlying processes
- data with which to force models and which can be assimilated into models to constrain and improve model parameterizations and formulations
- ability to capture synoptic scale (e.g., frontal) systems, which play a very important if not dominant role in large estuarine and coastal system inputs and responses.
- an estimate of scales of variability which are not accessible except via remote sensing (e.g. eddies, wind events, bloom dynamics)

It is important that the sea-going community request new and improved sensors. For example, the salinity mission will have impact on better determinations of global  $p\text{CO}_2$  patterns and variability and continued high quality ocean color, temperature, and vector wind observations are critical.

Satellite data cannot replace field observations, but they play a vital complementary role in extrapolating time and space relationships between AD-N and dust inputs and oceanic responses. Both field and remote sensing approaches are necessary to achieve the goals of understanding and quantifying global patterns in CRCs.

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